

Combinatorial Tools for the Production of Inorganic Thin Films*

Peter K. Schenck and Debra L. Kaiser
Ceramics Division
Materials Science and Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland, USA

The combinatorial chemistry approach to research has been utilized by the pharmaceutical industry for decades for the discovery of new drugs. We, at the Materials Science and Engineering Laboratory of the National Institute for Standards and Technology (NIST), decided to try this approach to develop research tools that could be used to accelerate the discovery and optimization of thin film inorganic materials for use in advanced communications and electronics systems. The combinatorial approach to materials discovery involves four phases: experimental design, fabrication of samples (library preparation), measurement of properties with high throughput assays, and the data management of the results (informatics). We have been involved for the last several years in the first three phases of the combinatorial approach. Others, here at NIST and elsewhere, have been developing tools for the data acquisition, analysis and mining required to handle the large volumes of information generated by combinatorial research.

The use of the combinatorial approach, or multiple-sample concept for new materials discovery, was first advocated by Hanak at RCA Laboratories in 1970. Using radio frequency sputtering with dual and triple composition targets, he produced binary and ternary thin films in his search for new superconducting materials. Hanak's novel concept for accelerated R&D was not adopted for a quarter of a century due in part to the lack of high-powered computing needed to process and manage the information, and the lack of microanalysis tools to carry out the high throughput assays. In 1995, Xiang and coworkers at Lawrence Berkeley National Laboratory applied the combinatorial approach to the rediscovery of high temperature superconducting materials. Over the next several years, researchers across the world demonstrated the power of combinatorial methods to discover a host of inorganic materials, including phosphors, dielectrics and catalysts. Combinatorial libraries or arrays of samples are being produced by many techniques including sputtering, chemical vapor deposition, ink jetting, and robotic mixers. The most common variable in combinatorial studies is the composition of the sample, but it is also possible to vary the processing parameters.

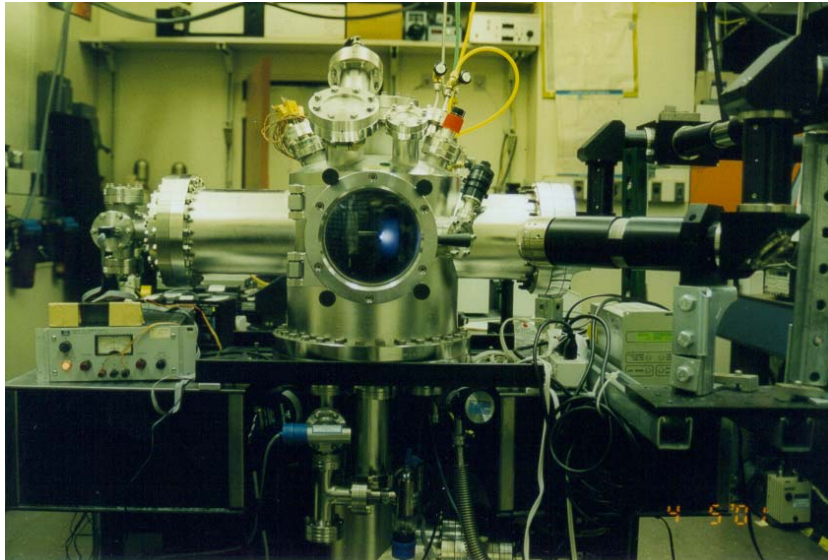
We decided to use pulsed laser deposition to produce our combinatorial films because researchers in our laboratory have had extensive experience with pulsed laser based research since the late 1980's. Our work originated in studies of the high temperature vaporization of materials using pulsed lasers, as a heating source, inside a mass spectrometer system. Using this container-less chemistry approach we were able to extend the vaporization data for several refractory materials to higher temperatures. This work was extended to using pulsed lasers to

*Published as "Blazing a Trail" in *Chemistry in Britain*, 39, May 2003, 45-47

Official contribution of the National Institute of Standards
and Technology, not subject to copyright in the United States.

vaporize target materials and deposit the vaporized species on a substrate to produce a thin film, a process known as pulsed laser deposition (PLD). Over the past decade, we have deposited a wide variety of inorganic films by PLD. In addition, we developed sophisticated diagnostic techniques for the characterization of the PLD process, including high-speed imaging and spectroscopy for the identification of species in the PLD plumes. This ability to monitor the PLD process provided the control capability we needed to extend our single beam, single target arrangement to a dual beam, dual target arrangement. With this novel arrangement, two different target materials can be deposited simultaneously to produce a combinatorial film with a composition gradient.

Our original PLD system consisted of an excimer laser, single beam delivery system and a vacuum chamber containing a target holder and a substrate heater. The original beam delivery system included beam alignment and steering optics, and an adjustable telescope for focusing the laser energy onto the target. From our studies of the PLD process, we had determined how the deposition rate and spatial distribution vary with the spot size of the laser, energy density (fluence) of the laser, and background pressure in the deposition chamber. We also had learned that target variations such as density could affect the deposition process.



Dual beam dual target PLD Apparatus

With this knowledge, we developed a plan for converting the single beam delivery system to a dual beam, dual target system suitable for fabricating combinatorial libraries. This experimental design phase of our work addressed three major components of the PLD apparatus: the beam delivery system, the target assembly, and the substrate heater. For the beam delivery system, we decided to replicate the capabilities of the single beam delivery system into a second delivery arm, allowing complete control of the spot size and energy on the second target. This design

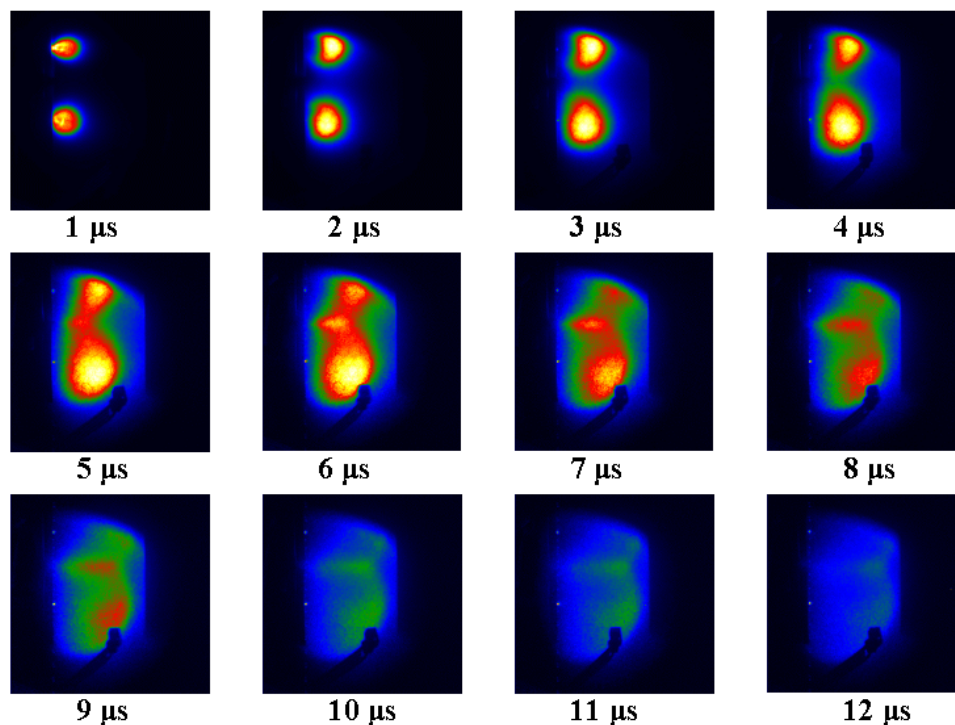
permits control of the deposition rate and distribution from each target to achieve the desired composition and thickness of the combinatorial library films. A laser beam diverter was used to divide the single incoming laser beam into two beams. The use of a variable beam diverter allows us to apportion the energy as required between the two targets. Further fine-tuning of the dual PLD process is accomplished with a variable attenuator in the second delivery arm. The deposition chamber, based on a standard surface analysis chamber, had an additional port at right angles to the original port used in the single beam system. By using this port, the chamber modifications were limited to retrofitting a crystal quartz window (required to accommodate the high energy ultraviolet laser beam) to the second beam entry port.

In addition to the beam delivery system, it was necessary to design a dual target system. Our original single target holder allowed for the rotation of the target, and a lateral back and forth motion of the target. With this holder design, the laser beam impacted on most of the target's front surface, and the direction of the laser beam attack on the target varied, preventing the development of surface roughness that could result in undesirable particulate formation. This target assembly was driven via rotating feedthroughs, which proved to be unreliable. In designing the dual target holder, we decided to use commercially available miniature vacuum compatible translation and rotation stages. The two rotation stages are mounted next to each other and attached to two linear stages configured to give motion up and down and back and forth relative to the laser impact points. This motion emulates the motion of the original single target assembly. The whole dual target holder occupies a volume less than 13 centimeters on a side.

The last design component is the holder for the substrate wafer onto which the species vaporized from the target deposit to build up the thin film. The substrate is heated to allow some diffusion of the vapor species to form a dense, homogeneous film. The substrate holder consists of a miniature flat heater and is positioned nominally three centimeters in front of the targets. A heat shield and extender arms attached to the rotation stages prevent the stages from becoming overheated. A computer is used to control the motion of the target holders, temperature of the heater, and monitor the temperature of critical components in the chamber.

During the library film preparation phase of our work, we chose the barium titanate (BaTiO_3) – strontium titanate (SrTiO_3) system (BST) as the first test system for the modified apparatus. The BST system is of interest for its dielectric and ferroelectric properties, particularly for wireless communication applications. We had deposited many barium titanate films using our original single beam delivery PLD system, and had also grown BST films of varying composition by metal organic chemical vapor deposition. Based on our earlier measurements of the deposition pattern obtained from PLD-deposited barium titanate and computer simulations of a dual deposition from two targets, we adjusted the focus of the two laser beams and the separation of the two laser spots on the targets. The deposition energy for each target was fine tuned by using the high speed imaging system. This system allowed us to monitor the size and progress of the plumes as they moved from the target to the substrate during the deposition process. Using this diagnostic tool, we adjusted the energies for comparable-sized plumes. The film was deposited on a heated silicon wafer with a low-pressure (13 Pascal) oxygen atmosphere to help maintain the oxygen balance in the film. In order to verify the composition gradient in the test film (measurement phase of the project), we engaged coworkers in NIST's Chemical Science and

Technology Laboratory. Using an electron probe microanalyzer they mapped the barium and strontium concentrations across the center of the two-centimeter film. They found that the barium to strontium ratio varied smoothly from 6.5 to 0.5 across the film, in good agreement with the computer simulations.



Sequence of false color images, intensity encoded, of the dual plume deposition of BST. The field of view is six centimeters with a target-substrate separation of three centimeters.

In order to expedite the fine-tuning of the combinatorial PLD process we developed our own capability to characterize the composition and uniformity (thickness) of the BST films. Our scanning spectroscopic reflectometry apparatus consists of a miniature fiber optic coupled commercial spectrometer and a computer controlled x-y stage. This apparatus has a spatial resolution of less than one-millimeter and a data collection/analysis time of 4-5 sec/point. We used the apparatus to map the thickness and optical properties of single target PLD films of barium titanate and other inorganic films. The thickness maps from single target PLD films were fit to a bimodal, in X and Y, cosine to the N distribution function. The bimodal distribution is required as the excimer laser beam is wider than high, resulting in an ellipsoidal deposition pattern that is tighter in width than height. These results on single target PLD films were used in the computer simulations during the experimental design phase of the combinatorial project.

We also characterize our combinatorial films using the scanning reflectometer. Results on one of the first combinatorial films indicated that the thickness at the barium rich side of the film was up to a factor of two less than the thickness at the strontium rich side of the film. From this result

it was apparent that we needed a better way to fine-tune the dual PLD process, since the apparent plume intensity is much greater for the strontium titanate plume than the barium titanate plume. In order to equalize the deposition rates from the two targets, we replaced the substrate holder with a dual deposition rate monitor (crystal quartz monitor). One of the two monitors was centered on each of the two targets. The laser energy distribution was then adjusted to nearly equalize the deposition rates. Films deposited under the adjusted conditions were much more uniform in thickness.

We decided that the spectroscopic reflectometer characterization of the film thickness might also be used for composition prediction. We made a series of test films on cold Si wafers using first only the barium titanate target, then only the strontium titanate target, and lastly both targets. After we mapped the thickness of the three films, we determined that the thickness pattern obtained from the sum of the single deposition target patterns was nearly the same as the thickness pattern obtained when both targets were used. As a result of this agreement, we can use the single target deposition patterns to accurately predict the composition gradient in a combinatorial PLD film. This result is consistent with Hanak's results using sputtering, where he observed that the sum of individual depositions was the same as his multiple-target deposition.

Since the early work on the BST system we have also used the combinatorial PLD system to deposit gold-nickel and gold-nickel oxide graded films. Gold-doped nickel oxide is a candidate material for transparent electrodes in optoelectronic devices. When annealed in air, the gold-nickel films become gold-nickel oxide graded films. These films are characterized for their transparency and conductivity by our collaborators outside NIST.

Since PLD is a versatile tool that can be used to deposit a wide range of complex inorganic materials, our dual beam-dual target PLD system may be used to deposit many graded composition combinatorial film libraries for discovery and optimization of multicomponent materials for advanced electronic, optoelectronic, and magnetic applications.

Further Reading

J. J. Hanak. *Journal of Materials Science*, 1970, **5**, 964.

X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W.G. Wallace-Freedman, S.-W. Chen, and P.G. Schultz, *Science*, 1995, **268**, 1738.

H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry A User's Guide*, New York, Wiley-Interscience, 1999.

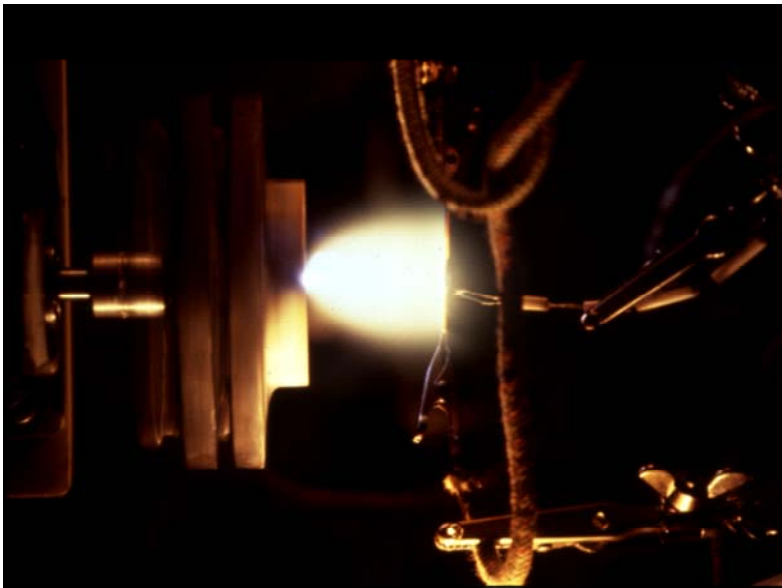
D. B. Chrisey and G. K. Hubler, editors, *Pulsed Laser Deposition of Thin Films*, New York, Wiley-Interscience, 1994.

<http://polymers.msel.nist.gov/combi/index/html>

<http://www.ceramics.nist.gov/programs/thinfilms/combi.htm>

Pulsed Laser Deposition

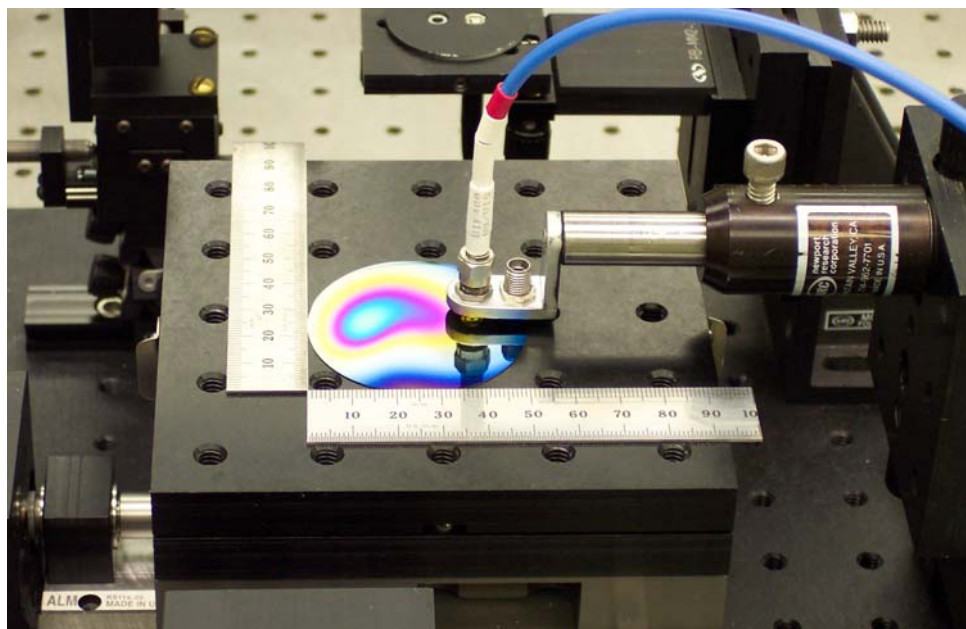
Pulsed laser deposition (PLD) involves the use of a high power pulsed laser to vaporize a target in a near vacuum. The plume of material vaporized from the target moves towards a substrate on which it deposits as a thin film. The technique was utilized early in the 1960's when the first pulsed ruby lasers were used to make metallic films. The technique received very little attention until the late 1980's when high temperature ceramic superconductors were discovered and it was found that these materials could be deposited as thin films using the PLD technique with ultraviolet light from excimer lasers. Since then, the technique has proven to be a good prototyping tool for making thin films of complex materials. The advantage of PLD for this purpose stems from the fact that the material is congruently vaporized from the surface of the target ensuring that the stoichiometry of the target is preserved in the plume generated by the laser. This stoichiometry is then preserved in the deposited thin film. In the case of gaseous species released from the target, the stoichiometry of the film can be preserved by carrying out the PLD process at a low pressure (13 Pascal or $\sim 10^{-4}$ atm.) of the gaseous species. In some cases, the starting target's composition can be adjusted to achieve the desired film composition. Since the process is inherently a high-energy process, the deposition rates are high and the substrate temperature can be lower than in other deposition techniques. The disadvantage of PLD is that the area coverage is generally small, a few square centimeters; however, this is not an issue for prototype films. Another difficulty with PLD is the production of particulates on the film. The most common sources of particulates are condensates produced in a high-density plume and solid masses removed directly from the target. The latter can be minimized by rastering and rotating the target and by using targets with densities greater than 90% of ideal density.



Highly energetic plume formed during the pulsed laser deposition process

Spectroscopic Reflectometry

Spectroscopic Reflectometry can be used to determine the thickness of thin nearly transparent films on both absorbing and transmitting substrates. The technique generally involves illuminating the film-on-substrate species with broadband light and collecting the reflected light normal to the surface into a spectrometer. A common arrangement is to use a dual (or bifurcated) fiber optic probe. This brings the light to the surface from a light source with one fiber and collects the reflected light for the spectrometer with the other. If a known reflective surface is used for reference, the source and spectrometer wavelength variations can be removed. Using sources and spectrometers with wavelength coverage in the near UV to near IR (250-1000 nm), film thickness and index of refraction can be measured for films ranging from tens of nanometers to several micrometers thick. The origin of the reflection spectra is called thin film interference, which is also the source of the colors seen when an oil slick forms on water. It is due to the interference between light reflected off the front and back surfaces of the film. In spectroscopic reflectometry, the reflection spectra obtained are oscillatory with wavelength. To first order the periodicity of the oscillations is proportional to the product of the film thickness and the index of refraction of the film. The depth of the oscillations is a function of the index of refraction of the film and the index of refraction of the substrate. There are, however, other complications: first the index of refraction is a complex number having two parts. The real part of the index of refraction is what we commonly refer to as the index; it is the ratio of the speed of light in a vacuum to the speed of light in the film. The imaginary part of the index is related to the absorption coefficient of the light in the fiber. Furthermore, both parts of the index of refraction exhibit dispersion, or a variation with wavelength. If the index of the film and substrate are well known, then the thickness of the film can be determined easily. If the index of the film is unknown, and it is dispersive, then the extraction of thickness and index from the reflection spectrum becomes more difficult. Typically in such cases appropriate models for the dispersion can be used to fit the spectrum. If the film thickness varies over the substrate, it can be mapped by mounting the substrate on a translation stage recording the reflection spectra as a function of position. This data can then be analyzed to extract thickness and index of refraction variations of the film.



Apparatus for measuring the thickness of a $\text{BaTiO}_3\text{-SrTiO}_3$ film